

ORGANOSILOXANES

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of the following applications: a) U.S. application Ser. No. 09/609,437 filed on Jun. 30, 2000 now U.S. Pat. No. 6,358,559, which is a divisional of Ser. No. 09/227,035 filed Jan. 7, 1999, now U.S. Pat. No. 6,177,199 issued on Jan. 23, 2001; b) U.S. application Ser. No. 09/609,499 filed on Jun. 30, 2000, now U.S. Pat. No. 6,361,820 which is a divisional of Ser. No. 09/227,498, filed Jan. 7, 1999, now U.S. Pat. No. 6,218,020 issued on Apr. 17, 2001; c) U.S. application Ser. No. 09/610,567 filed on Jul. 3, 2000, now U.S. Pat. No. 6,359,099, which is a divisional of Ser. No. 09/044,831, filed Mar. 20, 1998, now U.S. Pat. No. 6,218,497 issued on Apr. 17, 2001; d) U.S. application Ser. No. 09/611,528 filed on Jun. 30, 2000, now U.S. Pat. No. 4,512,070, which is a divisional of Ser. No. 09/044,798, filed Mar. 20, 1998, now U.S. Pat. No. 6,143,855 issued on Nov. 7, 2000; and e) U.S. application Ser. No. 10/078,919 filed on Feb. 19, 2002 (claiming the benefit of pending provisional patent applications U.S. Ser. No. 60/334,169 filed Nov. 20, 2001; U.S. Ser. No. 60/334,172 filed Nov. 29, 2001; and U.S. Ser. No. 60/336,662 filed Dec. 3, 2001, all of which are incorporated herein by reference in their entireties.

FIELD OF THE INVENTION

The present invention relates to semiconductor devices, and in particular, to semiconductor devices having low dielectric constant materials therein.

BACKGROUND OF THE INVENTION

In an effort to increase the performance and speed of semiconductor devices, semiconductor device manufacturers have sought to reduce the linewidth and spacing of interconnects while minimizing the transmission losses and reducing the capacitive coupling of the interconnects. One way to diminish power consumption and reduce capacitance is to decrease the dielectric constant (also referred to as "k") of the insulating material, or dielectric, that separates the interconnects. Insulator materials having low dielectric constants are especially desirable, because they typically allow faster signal propagation, reduce capacitance and cross talk between conductor lines, and lower voltages required for driving integrated circuits. Therefore, as interconnect linewidths decrease, concomitant decreases in the dielectric constant of the insulating material are required to achieve the improved performance and speed desired of future semiconductor devices. For example, devices having interconnect linewidths of 0.13 or 0.10 micron and below seek an insulating material having a dielectric constant (k) < 3. Semiconductor device manufacturers also seek materials that in addition to having a low dielectric constant, have the mechanical and thermal stability needed to withstand the thermal cycling and processing steps of semiconductor device manufacturing.

In a typical damascene process, a line pattern is etched in the surface of a insulating material, and the trenches formed in this manner, i.e., the horizontal structure created to house the horizontal electrical connections within a particular level or layer in a semiconductor device, is filled with copper by electroplating, electroless plating, or sputtering. After the copper is deposited onto the entire surface, a chemical-mechanical planarization (CMP) step is employed to remove excess copper, and to planarize the wafer for subsequent

processing steps. This process is typically repeated several times to form vias, i.e., the vertical structures created to contain the vertical electrical connections that connect the trenches between at least two metal levels or layers of metal in a semiconductor device.

To further improve the damascene process, via and line formation can be integrated into a single process, which is then called dual damascene process. In the dual damascene process, a via dielectric layer is laid down onto a substrate, and the via dielectric layer is subsequently coated with a patterned etch stop layer, i.e., a layer that controls the etching or removal of the dielectric, whereby voids in the etch stop layer correspond to positions of vias that will be etched into the via dielectric. In a next step, a line dielectric is deposited onto the etch stop layer, which in turn is coated with a patterned hardmask layer that defines the traces of the lines. Current hardmask layers are made of silicon nitride, silicon oxynitride, silicon oxide, or silicon carbide. In a following step via and line traces are formed, whereby the line trenches are etched into the line dielectric until the etchant reaches the etch stop layer. In positions where there is no etch stop layer, the etching process continues through the via dielectric to form a via. As in the damascene process, etched via and line traces are filled with copper (after applying a Ta(N) barrier layer and a Cu-seed layer) and a CMP step finishes the dual damascene process.

Dielectric etching is difficult to control with today's required trench width of 0.13 micron. Thus, the etch stop performs a critical role in semiconductor device construction. A disadvantage of known hardmask and etch stop materials is their relatively high dielectric constant (k-value). For example, typical hardmask and etch stop materials, including SiN, SiON, SiO₂, and SiC, have an undesirably high dielectric constant of at least about 4.0 and are applied by chemical vapor deposition (CVD). Although J. J. Waeterloos et al., "Integration of a Low Permittivity Spin-on Embedded Hardmask for Cu/SiLK Resin Dual Damascene", Proceedings of the IEEE 2001 International Interconnect Technology Conference, pages 60-62 (Jun. 4-6, 2001) teaches that a low-k spin-on organosiloxane film may replace the preceding known etch stop materials to lower the effective k value, the article reports that the organosiloxane film has a k value of 3.2 and does not disclose any details about the organosiloxane used.

U.S. Pat. No. 4,626,556 teaches organosilsesquioxane having required alkyl and alkenyl group side chains bonded thereto and optionally aryl groups and hydrogen side chains bonded thereto as a substitute for a photoresist material. U.S. Pat. No. 4,626,556 does not teach that its organosilsesquioxane may function as an etch stop or hardmask. In Comparative A below, we made an organosilsesquioxane having the required minimum at least 50% methyl groups of U.S. Pat. No. 4,626,556 and this material did not wet known dielectric materials and thus, would not be useful as an etch stop. Although U.S. Pat. No. 4,626,556 teaches that its organosilsesquioxane films have low dielectric constants, U.S. Pat. No. 4,626,556 does not report any dielectric constant values. However, as those skilled in the art know, silanol results in an undesirable dielectric constant and U.S. Pat. No. 4,626,556's organosilsesquioxane transmission FTIR plots show that silanol (3400-3700/cm) is present. Also, U.S. Pat. No. 4,626,556 teaches in a preferred embodiment, the presence of a crosslinking agent that is light activated and as those skilled in the art know, that these materials have high dielectric constants. Also, U.S. Pat. No. 4,626,556 teaches that at least 50% of its side chains are alkyl groups since the larger the amount of the alkyl group

present, the higher the heat resistance U.S. Pat. No. 4,626, 556's Examples 13 and 14 teach that its organosilsesquioxane was applied to a two inch thick silicone wafer wherein a thin film of one micron was formed; the film was then heated at 250° C. for 2 hours, at 350° C. for 1 hour, and then at 450° C. for 30 minutes, and subjected to thermogravimetric analysis, in which no weight loss was observed up to 600° C. It is not clear if the silicone wafer weight was included in the "no weight loss" reported. Today's semiconductor manufacturers require a more stringent TGA test of a film alone and not on a wafer. This current more stringent TGA test requires heating and holding at 200° C. (Weight loss represents how well the material was dried.), holding at 430° C. for 90 minutes (Weight loss represents worst case scenario for shrinkage from low temperature bake to high temperature cure.), and heating at 450° C. (Weight loss represents thermal stability.). Thus, U.S. Pat. No. 4,626, 556's organosilsesquioxane does not have the wetting characteristics, low dielectric constant, and thermal stability required by today's semiconductor manufacturers.

In 1999, AlliedSignal Inc., now Honeywell International Inc., introduced HOSP® product comprising organosiloxane having about 80% methyl groups and 20% hydrogen groups. US Patent Publication 2001/006848A1 published Jul. 5, 2001 teaches that AlliedSignal's HOSP™ product is useful as a hardmask. Unfortunately, as reported in Comparative A below, this product does not have acceptable wetting properties with organic dielectrics.

Commonly assigned U.S. Pat. Nos. 5,973,095; 6,020,410; 6,043,330; 6,177,143; and 6,287,477 teach organohydridosiloxane resins of the formula $(H_{0.4-1.0}SiO_{1.5-1.8})_n(R_{0.4-1.0}SiO_{1.5-1.8})_m$ where R is alkyl groups, aryl groups, and mixtures thereof. See also commonly assigned U.S. Pat. No. 6,015,457. Unfortunately, as reported in Comparative B below, a composition comprising 50% phenyl groups and 50% hydrogen subjected to the current stringent TGA test had a weight loss of 1.0 percent per hour.

Thus, a need still exists in the semiconductor industry to provide: a) compositions with lower dielectric constants; b) compositions with improved mechanical properties, such as thermal stability, glass transition temperature (T_g), and hardness; c) compositions that are capable of being solvated and spun-on to a wafer or layered material; and d) compositions that are versatile enough to function as a hardmask or an etch stop and can wet dielectric materials.

SUMMARY OF THE INVENTION

In response to this need in the art, the present invention provides an organosiloxane comprising at least 80 weight percent of Formula I: $[Y_{0.01-1.0}SiO_{1.5-2}]_a[Z_{0.01-1.0}SiO_{1.5-2}]_b[H_{0.01-1.0}SiO_{1.5-2}]_c$ where Y is aryl; Z is alkenyl; a is from 15 percent to 70 percent of Formula I; b is from 2 percent to 50 percent of Formula I; and c is from 20 percent to 80 percent of Formula I. Unlike alkyl-containing materials similar to those taught in U.S. Pat. No. 4,626,556 that do not wet known dielectric materials, the present composition wets dielectric materials as reported in our Examples below and thus, may be advantageously used as an etch stop. Contrary to U.S. Pat. No. 4,626,556's teaching that its organosilsesquioxane requires the presence of alkyl groups for heat resistance and does not require the presence of aryl groups, we have discovered that the present composition requiring the presence of aryl groups but not requiring the presence of alkyl groups has good thermal stability as evidenced by the TGA results reported below. The present composition also has a dielectric constant of preferably less than 3.2. Another

benefit of the present composition is that it has a low crosslinking temperature. The present composition may contain up to 20 weight percent of other units as long as the other units do not detract from the desirable properties of the present composition.

In another embodiment, the present invention provides a spin-on etch stop comprising organosiloxane of Formula I: $[Y_{0.01-1.0}SiO_{1.5-2}]_a[Z_{0.01-1.0}SiO_{1.5-2}]_b[H_{0.01-1.0}SiO_{1.5-2}]_c$ where Y is aryl; Z is alkenyl; a is from 15 percent to 70 percent of Formula I; b is from 2 percent to 50 percent of Formula I; and c is from 20 percent to 80 percent of Formula I and having substantially no silanol and a dielectric constant of less than 3.2. This etch stop advantageously wets dielectric materials, has good adhesion to dielectric materials, has good thermal stability, and a low crosslinking temperature.

In another embodiment, the present invention provides an organosiloxane having alkenyl groups and thermal stability.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows TGA data for Honeywell Accuglass® 720 organosiloxane comprising 66% phenyl and 34% methyl.

FIG. 2 shows TGA data for Honeywell HOSP® organosiloxane having 80% methyl groups and 20% hydrogen.

FIG. 3 shows TGA data for organosiloxane having 50% phenyl groups and 50% hydrogen.

FIG. 4 shows TGA data for the present composition.

FIG. 5 shows FTIR data for the present composition.

DETAILED DESCRIPTION OF THE INVENTION

The phrase "substantially no silanol" as used herein excludes the presence of silanol as evidenced by FTIR silanol peaks taught by U.S. Pat. No. 4,626,556.

The term "organosiloxane" as used herein means Si and carbon containing compounds, includes organosilsesquioxane, and excludes the presence of crosslinking agent activated by light as taught by U.S. Pat. No. 4,626,556.

The phrase "thermal stability" as used herein means less than 0.5 percent weight loss at 450° C.

Contemplated polymers comprise a polymer backbone encompassing alternate silicon and oxygen atoms. In Formula I above, preferably Y is phenyl, benzyl, substituted phenyl, naphthyl, anthryl, and phenanthryl. In Formula I above, preferably Z is vinyl, substituted vinyl, vinyl ether, acrylate, and methacrylate. In Formula I above, preferably a is from 30 percent to 70 percent of Formula I and b is from 10 percent to 40 percent of Formula I.

Polymers of the present invention may be produced with or without essentially no hydroxyl or alkoxy groups bonded to backbone silicon atoms. Preferably, each silicon atom, in addition to the aforementioned backbone oxygen atoms, is bonded only to hydrogen atoms and/or Y groups or Z groups as defined in Formula I. By attaching only hydrogen and/or Y and Z groups directly to backbone silicon atoms in the polymer, unwanted chain lengthening and cross-linking is avoided. And given, among other things, that unwanted chain lengthening and cross-linking is avoided in the resins of the present invention, the shelf life of these resin solutions is enhanced as compared to previously known organosiloxane resins. Furthermore, since silicon-carbon bonds are less reactive than silicon-hydrogen bonds, the shelf life of the organosiloxane resin solutions described herein is enhanced as compared to previously known hydridosiloxane resins.

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Preferably, the present organosiloxane has a molecular weight from about 1,000 to about 100,000.

In a preferred embodiment, it is believed but not confirmed that the polymer backbone conformation is a cage configuration. Accordingly, there are only very low levels or reactive terminal moieties in the polymer resin given the cage conformation. A cage conformation of the polymer backbone also ensures that no unwanted chain lengthening polymerization will occur in solution, resulting in an extended shelf life. Each silicon atom of the polymer is bonded to at least three oxygen atoms. Moieties bonded to the polymer backbone include hydrogen and the organic groups described herein.

The present organosiloxane composition may be made with a dual phase solvent system using a catalyst. The starting materials encompass trichlorosilane and a combination of organotrichlorosilanes including alkenyl or aryl substituted trichlorosilane. The relative ratios of the trichlorosilane and the organotrichlorosilane determine the mole percent carbon-containing substituents in the polymer. As an example, the method is as follows. Mix a solution of hydridotrihalosilanes and organic-substituted trihalosilanes (e.g. trichlorosilane and alkenyl or aryltrichlorosilane) to provide a mixture. Combine the mixture with a dual phase solvent including a non-polar solvent, and a polar solvent to provide a dual phase reaction mixture. Add a solid phase catalyst to the silane/solvent reaction mixture. React the silanes to produce organohydridosiloxanes. Recover the organosiloxane from the organic portion of the dual phase solvent system. Additional steps may include washing the recovered organosiloxane to remove any unreacted monomer, and fractionating the organosiloxane product to thereby classify the product according to molecular weight.

A catalyst used as a phase transfer catalyst may be used such as tetrabutylammonium chloride, and benzyltrimethylammonium chloride. The phase transfer catalyst is introduced into the reaction mixture and the reaction is allowed to proceed to the desired degree of polymerization.

A dual phase solvent system including a continuous phase non-polar solvent and a polar solvent may be used. The non-polar solvent includes, but is not limited to, any suitable alkyl, alkenyl or aryl compounds or a mixture of any or all such suitable compounds, the operational definition of "suitable" in the present context includes the functional characteristics of: 1) solubilizing the monomeric silicon compounds, 2) solubilizing the resin product, 3) stability of the resin product in the solvent, and 4) insolubility of unwanted reaction products.

Contemplated solvents include any suitable pure or mixture of organic, organometallic or inorganic molecules that are volatilized at a desired temperature, such as the critical temperature. The solvent may also comprise any suitable pure or mixture of polar and non-polar compounds. In preferred embodiments, the solvent comprises water, ethanol, propanol, acetone, ethylene oxide, benzene, toluene, ethers, cyclohexanone, butyrolactone, methylethylketone, and anisole. As used herein, the term "pure" means that component that has a constant composition. For example, pure water is composed solely of H₂O. As used herein, the term "mixture" means that component that is not pure, including salt water. As used herein, the term "polar" means that characteristic of a molecule or compound that creates an unequal charge, partial charge or spontaneous charge distribution at one point of or along the molecule or compound. As used herein, the term "non-polar" means that characteristic of a molecule or compound that creates an

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equal charge, partial charge or spontaneous charge distribution at one point of or along the molecule or compound. Particularly preferred solvents include, but are not limited to, pentane, hexane, heptane, cyclohexane, benzene, toluene, xylene, halogenated solvents such as carbon tetrachloride, and mixtures thereof.

The second solvent phase is a polar phase, immiscible with the organic, non-polar solvent phase, and includes water, alcohols, and alcohol and water mixtures. It is thought that alcohol solubilizes reactive intermediates that are not yet soluble in the non-polar phase and would ordinarily be unstable in a substantially aqueous phase. The amount of alcohol present is, however, not so high as to significantly dissolve product polymers having molecular weights greater than about 400 AMUs.

Alcohols and other polar solvents suitable for use in the polar phase include, but are not limited to, water, methanol, ethanol, isopropanol, glycerol, diethyl ether, tetrahydrofuran, diglyme, and mixtures thereof. In one embodiment, the polar solvent includes a water/alcohol mixture wherein the water is present in an amount sufficient to preferentially solubilize ionic impurities not soluble in alcohol, and/or preclude solvent extraction of product compounds that might otherwise be soluble in alcohol. The polar solvent phase advantageously retains the hydrochloric acid (HCl) condensation product and any metal salt or other ionic contaminants that may be present. Since any ionic contaminants are retained in the polar solvent phase, the organosiloxane product of this invention is of high purity and contains essentially no metal contaminants.

In another embodiment of the method disclosed herein, a solid phase catalyst and/or ion exchange resin, such as the Amberjet 4200 or Amberlite I-6766 ion exchange resins (both available from Rohm and Hass Company, Philadelphia, Pa.), surface catalyzes the polymerization of the trihalosilane and organo-trihalosilane monomers into the composition of this invention. Amberjet 4200 is a basic anion exchange resin based on the chloride ion. Amberlite I-6766 is also a basic anion exchange resin. By way of explanation, and not by way of limitation, it is thought polymer chain propagation occurs on the catalyst surface by hydrolysis of the Si—Cl bond of the monomer to Si—OH, followed by condensation with another Si—OH to provide an Si—O—Si bond, thereby extending the polymer chain. In other embodiments, polymerization is catalyzed with a phase transfer catalyst such as tetrabutylammonium chloride.

The resulting siloxane/solvent solution is then filtered under ambient conditions via any of the filtration devices well known in the art. It is generally preferable to use a filtration device having a pore size less than about 1 m. A typical filtration process uses a pore size of about 0.1 m. Utility:

The present organosiloxane may also comprise additional components such as adhesion promoters, antifoam agents, detergents, flame retardants, pigments, plasticizers, stabilizers, striation modifiers, and surfactants.

The present organosiloxane may be used as ceramic binder, high temperature encapsulant, and fiber matrix binder. The present composition is also useful as an adhesion promoter in that it exhibits good adhesive properties when coupled with other materials in non-microelectronic or microelectronic applications. In microelectronic applications, the present composition may be coupled with conventional and not-so-conventional layered materials, such as nanoporous dielectrics, cage-based dielectric materials, anti-reflective coatings, photoresist materials,